A New Sulphonic Acid Functionalized Periodic Mesoporous Organosilica as a Suitable Catalyst

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Abstract

A new solid acid catalyst is developed by the direct sulphonation of the ethene bond of a pure trans ethene bridged Periodic Mesoporous Organosilica. The catalytic activity of this mesoporous material is evaluated in an esterification reaction and compared with *p*-toluenesulphonic acid. The sulphonated ethene PMO can compete with a homogeneous catalyst and maintains its porosity.

Keywords: Solid Acid Catalyst, Periodic Mesoporous Organosilica, Esterification.

1. Introduction

Esterifications are key reactions in the manufacturing of chemicals[1] and mostly they require an acid catalyst[2]. Although homogeneous catalysts are still widely used, they exhibit a major disadvantage, as they cannot be easily separated from the reaction mixture, and are therefore not appropriate for continuous flow procedures. Heterogeneous catalysts are effortlessly recovered from the reaction mixture, but the recyclability of the catalyst is a very important additional parameter.

Functionalized Periodic Mesoporous Organosilicas[3] (PMOs) can act as a solid acid catalyst. PMOs exhibit large specific surface areas, pore diameters of 2-50 nm and narrow pore size distributions. They are mostly synthesized with bridged bis-silanes with a general structure $(EtO)_3$-Si-R-Si-$(OEt)_3$ (Figure 1)[4]. This bis-silane polycondensates around a template such as the surfactant P123 $(EO)_{20}(PO)_{70}(EO)_{20}$. After formation of the PMO, the template is removed by an extraction to reveal the pores of the hybrid material[5].

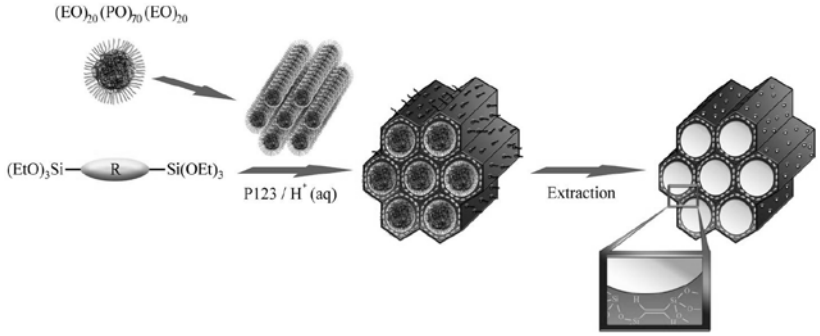

Figure 1. Synthesis of a Periodic Mesoporous Organosilica. R represents an organic functionality such as -CH=CH-.

One of the most important advantages of functionalized ethene PMOs is the fact that the functionalization occurs by the addition and substitution to the ethene double bond,

creating a C-C grafing as opposed to a Si-O-C grafing in the case of silica materials. The C-C grafting renders the functionalized materials very stable towards hydrolysis. In this case, the PMOs are modified to attain a sulphonic acid group and transform these materials into suitable solid acid catalysts. These catalysts can be straightforwardly removed from the reaction mixture and in addition, they can be regenerated with a acidic solution and reused in multiple catalytic cycles.

Introducing the sulphonic acid functionality can be performed via different pathways. Pioneering work has been done by Nakajima and Kondo[6]. Via a Diels-Alder reaction with benzocyclobutene, they introduced a benzene moiety and afterwards they performed a sulphonation. They achieved an acidity of 1.44 mmol H^+/g. Other reports[7-9] describe the preparation of a solid catalyst by the co-condensation or grafting with 3-mercaptorpropyltriethoxysilane which is subsequently oxidized by H_2O_2, H_2SO_4 or HNO_3.

This study presents the synthesis of an ethene PMO functionalized with $–SO_3H$ moieties. The solid acid catalyst is prepared via a direct sulphonation of the ethene bond of a pure trans ethene PMO[6] (Figure 2). This material is prepared with a homemade precursor[8] described by our group before. After characterization, esterification experiments are performed to evaluate the catalytic activity of the solid acid catalyst.

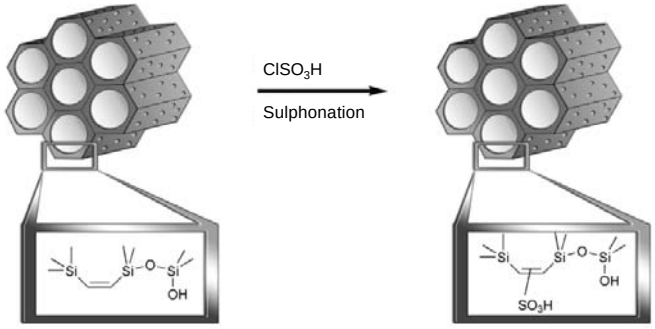

Figure 2. Sulphonation process of the trans ethene bridged PMO.

2. Experimental Section

The pure trans 1,2-bis(triethoxysilyl)ethene (E-BTSE) and pure trans ethene bridged PMO (E-ePMO) are prepared according to the procedures published by our group[5, 10]. The sulphonation of ePMO is performed with chlorosulphonic acid (E-ePMO-SO_3H). In a typical synthesis, 20 ml of dry CH_2Cl_2 is added to the dried ePMO under an inert atmosphere and cooled with an ice bath. 4.5 ml of chlorosulphonic acid is added. The reaction is stirred for 24 hours. Subsequently, the mixture is poured out in H_2O and the material is further washed until the pH of the filtrate is neutral. Finally, the sulphonated PMO (E-ePMO-SO_3H) is washed with methanol and acetone before drying the sample. The acidity of the sulphonated PMO is determined by a titration with NaOH (0.1 M). The catalytic activity of the materials is evaluated with the esterification of n-propanol with acetic acid. In a typical experiment, 4.9 ml toluene, 3.4 ml n-propanol, 3.86 ml acetic acid and 1.0 ml butyl acetate are added to the catalyst (0.207 g). The mixture is heated to 135°C while stirring. During the catalytic reaction, the formed water is constantly removed by a Dean-Stark setup. Samples of the mixture are taken at several point in time which are analyzed by GC.

3. Results and Discussion

The trans ethene bridged PMOs are sulphonated with chlorosulphonic acid and are characterized with nitrogen adsorption desorption experiments. The characteristics of the E-ePMO and the E-ePMO-SO_3H are presented in Table 1. The sulphonation process has no great influence on the porosity of the material. Only a slight increase in S_{BET} occurs after the treatment with chlorosulphonic acid.

Table 1. Properties of the ethene bridged PMOs before and after the sulphonation.

Sample	S_{BET} (m^2/g)[a]	V_t (cm^3/g)[b]	V_μ (cm^3/g)[c]	D_p (nm)[d]
E-ePMO	987	1.16	0.15	8.1
E-ePMO-SO_3H[e]	1047	1.18	0.18	8.1

[a] Surface area, [b] Total pore volume, [c] Micropore volume, [d] Pore diameter (calculated from adsorption isotherm with BJH method), [e] Sulphonation of the material for 24 h.

The acidity of the materials is determined with an acid base titration using sodium hydroxide. Approximately 0.69 mmol H^+ / gram material is observed when performing a sulphonation for 6 hours. A higher acidity of 1.08 mmol H^+/gram E-ePMO-SO_3H is observed when the reaction is performed for a longer period of time (24 hours).
The solid acid catalyst is evaluated by performing an esterification reaction (Figure 3) with acetic acid and n-propanol. Its catalytic activity is compared with a homogeneous catalyst *p*-toluenesulphonic acid (*p*-TsOH).

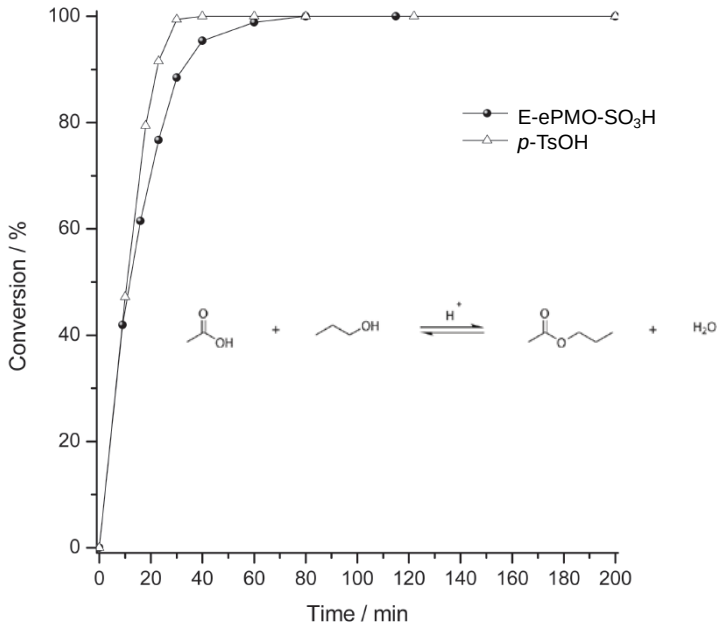

Figure 3. The esterification reaction of acetic acid with n-propanol is examined for *p*-toluene-sulphonic acid and E-ePMO-SO_3H. The conversions of n-propanol for both catalysts are presented in the graph.

The catalytic performance of the E-ePMO-SO_3H is shown in Figure 3. After 80 minutes, the E-ePMO-SO_3H with a catalyst loading of 0.49% reaches complete conversion. The p-toluenesulphonic acid with a loading of 0.45% obtains a conversion

of 100% after 40 minutes. Moreover, the turn-over-number (TON) of E-ePMO-SO_3H (204) resemble that of the homogeneous catalyst (222) Therefore the PMO exhibits a comparable catalytic activity as the homogeneous catalyst.

The stability of the heterogeneous catalyst is an important parameter. The porosity of the acidic PMO is investigated with nitrogen physisorption (Figure 4), where only a minor differences are observed. The specific surface area slightly decreases to 800 m^2/g with a pore volume of 0.98 cm^3/g and a pore size of 7.1 nm.

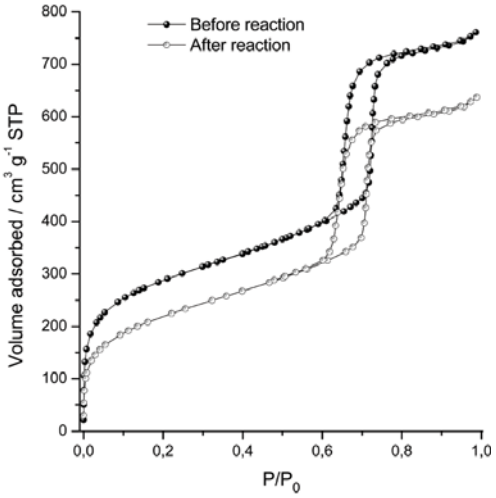

Figure 4. Nitrogen adsorption desorption isotherm of E-ePMO-SO_3H before and after reaction.

These preliminary catalytic results already show the potential of this solid acid catalyst in esterification reactions. In depth studies on the recyclability of the catalyst and alternative sulphonation procedures are currently ongoing.

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